J. Phys. Chem. A **2007,** *111,* 9509−9515

Pressure and Temperature Dependence of H-Atom Tunneling in the Debye Approximation. Barrier Preparation and Media Reorganization[†]

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Received: April 27, 2007; In Final Form: August 7, 2007

In the frame of the radiationless transitions modified theory, the analytical expression of a rate constant of the chemical reaction with an atom tunneling is found for the case of a continuous spectrum of a phonon subsystem. Two mechanisms of temperature dependence of a rate constant are taken into account, the oscillations of the potential barrier of the reaction at the intermolecular vibrations and media reorganization. The simple expressions for temperature and pressure dependencies of a rate constant are obtained in the special case of lattice motion—the Debye model. The well-known Marcus expression for the rate constant of an electron transfer in the Debye phonon spectrum is deduced first. The pressure dependence of the reorganization energy of the media is derived. Comparison of the theoretical results with the literature experimental data on H-atom tunneling in the fluorene−acridine crystal, taking into account four promotive modes (translational, librational, and two low-frequency intramolecular modes at 95 and 238 cm^{-1}) and the frequency dependence of the Grueneisen parameter, is fulfilled. Good agreement of the theory and experiments is observed.

I. Introduction

It is known that the pressure and temperature essentially affect the rate constant of H-atom tunneling in different chemical reactions.[1−4] A few processes were investigated in the condensed phase during last three decades.[1−20] The observation of the low-temperature limit of the rate constant was one of the main evidences of the tunneling mechanism of these reactions. At higher temperatures, the rate constant (k) of tunneling sharply increases and, after the region with linear dependence of the coordinates, ln $k - T$, becomes the Arrhenius-type curve (for the detailed description of the rate constant temperature dependence, see, for example, refs 1 and 21). The explanation of the low-temperature limit and other peculiarities of H-atom tunneling chemical reactions was given first in the refs 22−25. Later, these theoretical investigations were continued by different authors (these works are cited in refs 1, 2, and 4).

Briefly, the mechanism of the pressure and temperature dependence of the condensed-phase reactions with H-atom tunneling is discussed next. A rate constant of the H-atom tunneling is determined by the distance between reagents and the frequency of the intermolecular and soft intramolecular vibrations of the reagents. These values depend on the pressure and temperature.

The vibrations lead to oscillations of the distance between reagents. The higher the temperature, the larger the amplitude of thermal vibrations and the shorter the effective distance between the reagents, and consequently, the potential barrier is smaller. The probability of tunneling is larger if the barrier is smaller. Hence, the rate constant of transition increases with increasing temperature. Such oscillations changing the tunneling potential barrier are called promotive modes. At low temperatures, only low-frequency vibrations are thermally activated; therefore, they determine the temperature dependence of tunneling.

The pressure effect on the tunneling rate constant can be considered within the framework of the proposed model. It is clear that pressure can influence the tunneling distance as well as the promotive frequencies; the action of the pressure decreases the volume and the linear sizes of a monocrystal elementary cell. Consequently, the equilibrium distance between the reagents and the tunneling length decreases, and the probability of the tunneling sharply increases. Second, the frequencies of the promotive modes also depend on pressure and temperature due to anharmonicity.

Therefore, there are three characteristics of the tunneling curve presented in the coordinates ln $k - T$ which strongly depend on pressure.

1. The position of the low-temperature limit is determined by the distance between the reagents and increases when the distance between the reagents decreases under the pressure action.
2. The position of the point where the rate constant starts to grow with temperature according to the law $k \sim \exp[\alpha' T]$ (see eq 7) depends on the promotive vibrational frequencies. The increase of the frequency results in the shift of this point to the right. As discussed in section IV, the frequency increases with increasing pressure.
3. The tangent (α') of the angle of the slope of the ln $k(T)$ linear part (see formula above) is inversely proportional to the squares of the promotive frequencies. This value decreases with pressure.

Recently, in the example of the fluorene−acridine system, the temperature and pressure dependence of the rate constant of the low-temperature chemical reaction with H-atom tunneling were investigated theoretically[26,27] on the basis of the two-dimensional potential energy surfaces generated at the DFT-

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[†] Part of the "Sheng Hsien Lin Festschrift".

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10.1021/jp073258l CCC: $37.00

B3LYP/6-31G* level. In this paper, consideration of the solid-phase tunneling reactions will be continued. The analytical expressions for the rate constant are deduced in the framework of the Debye model of the lattice. Some updating of the comparison of the experimental and theoretical data will be conducted; in particular, the frequency dependence of Grueneisen parameters is taken into account.

II. Effect of Temperature on the Tunneling Rate Constant

In the frame of a modified theory of radiationless transitions,[1] within the double adiabatic approximation, accounting for the barrier oscillations at the intermolecular vibrations and media reorganization, the rate constant of atom tunneling is equal to

$$k = \frac{1}{\hbar}|V(R_0)|^2 \int_{-\infty}^{+\infty} \mathrm{d}t \exp\{-i\Delta E(t + i/2k_\mathrm{B}T) + \sum_\mu [(J'_\mu)^2/4 - (\Delta q_\mu)^2] \coth(\hbar\omega_\mu/2k_\mathrm{B}T)/2 + \sum_\mu [(J'_\mu)^2/4 + (\Delta q_\mu)^2] \cos(t\hbar\omega_\mu)/2 \sinh(\hbar\omega_\mu/2k_\mathrm{B}T) + i\sum_\mu J'_\mu \Delta q_\mu \sin(t\hbar\omega_\mu)/2 \sinh(\hbar\omega_\mu/2k_\mathrm{B}T)\}$$

$$J(R) = 2S(R)/\hbar = (2/\hbar) \int \{2m_\mathrm{H}[U(x,R) - E_\mathrm{H}(R)]\}^{1/2}\mathrm{d}x \qquad J'_\mu = \partial J/\partial q_\mu \quad (1)$$

In this formula, $V(R_0)$ is the interaction inducing the transfer; this matrix element is proportional to $\exp\{-S(R_0)\}$, where $S(R)$ is the quasiclassical action of the tunneling particle in the underbarrier space. ΔE is the defect of energy, k_B is the Boltzmann's constant, $\hbar$ is the Plank constant, and T is the Kelvin temperature. The parameters Δq_μ and $\hbar J'_\mu$ are the displacements of the phonon coordinates (q_μ) and the derivative of the doubled classical action ($S(R)$) of the tunneling particle in the underbarrier space.[1] The criterion of the double adiabatic approximation applicability is $2\pi/d\omega_0\sqrt{2U_0/m_H} \gg 1$ (U_0 and d are the height and width of the potential barrier for atom tunneling, ω_0 is the characteristic frequency of the promotive or reorganization modes, and m_H is the mass of the transferring particle).[1,21,28,29] The formula in eq 1 corresponds to the case $J'' = 0$ ($J'' = \partial^2 J/\partial x^2$). Indeed, in the temperature range where the inequality $k_\mathrm{B}T < \gamma_R/J''$ (γ_R is the force constant) obeys, the amplitude of intermolecular vibrations is small; therefore, it is possible[1] to consider the case of $J'' = 0$. At low temperatures for a continuous spectrum of the phonon subsystem, the values J'_μ and Δq_μ in the eq 1 are the degree functions of the frequency

$$J'_\mu(\omega) = a_1\omega^{p1} \qquad \Delta q_\mu(\omega) = a_2\omega^{p2} \qquad (2)$$

and the spectral density is

$$f(\omega) = a_3\omega^{p3}\exp\{-\omega/\omega_\mathrm{C}\} \qquad (2')$$

Here, a_1, a_2, and a_3 are constants; the exponent powers $p1$, $p2$, $p3 > 0$ are determined by the phonon spectrum of the considered system; ω_C is the frequency describing the region where the spectral density of the exponential function with the power $p3$ is defined.

Changing the summation on integration in eq 1

$$\sum_\mu \rightarrow \int_0^\infty f(\omega)\,\mathrm{d}\omega$$

and separating out the standard expressions for the Riemann Zeta function and the gamma function, one can find the tunneling rate constant for the continuous phonon spectrum

$$k = \frac{1}{\hbar}|V(R_0)|^2 \exp\left\{\frac{\Delta E}{2k_\mathrm{B}T}\right\} \exp\{F_1\} \int_{-\infty}^{+\infty} \mathrm{d}s \exp\{-i\Delta Es + F_2(s) + F_3(s)\}$$

$$F_1 = \frac{a_3{a_1}^2}{4}\left(\frac{k_\mathrm{B}T}{\hbar}\right)^{2p1+p3+1} \Gamma(2p1 + p3 + 1)\xi\left(2p1 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}}\right) - \frac{a_3{a_1}^2}{8}\omega^{2p1+p3+1}\Gamma(2p1 + p3 + 1) + \frac{a_3{a_2}^2}{2}\omega^{2p2+p3+1}\Gamma(2p2 + p3 + 1) - a_3{a_2}^2\left(\frac{k_\mathrm{B}T}{\hbar}\right)^{2p2+p3+1} \Gamma(2p2 + p3 + 1)\xi\left(2p2 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}}\right)$$

$$F_2(s) = \frac{a_3}{2}\frac{{a_1}^2}{4}\left(\frac{k_\mathrm{B}T}{\hbar}\right)^{2p1+p3+1} \Gamma(2p1 + p3 + 1) \times \left\{\xi\left(2p1 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} - ik_\mathrm{B}Ts\right) + \xi\left(2p1 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} + ik_\mathrm{B}Ts\right)\right\} + \frac{a_3}{2}{a_2}^2\left(\frac{k_\mathrm{B}T}{\hbar}\right)^{2p2+p3+1} \Gamma(2p2 + p3 + 1) \times \left\{\xi\left(2p2 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} - ik_\mathrm{B}Ts\right) + \xi\left(2p2 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} + ik_\mathrm{B}Ts\right)\right\}$$

$$F_3(s) = \frac{a_1a_2a_3}{2}\left(\frac{k_\mathrm{B}T}{\hbar}\right)^{p1+p2+p3+1} \Gamma(p1 + p2 + p3 + 1) \times \left\{\xi\left(p1 + p2 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} - ik_\mathrm{B}Ts\right) + \xi\left(p1 + p2 + p3 + 1,\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{C}} + \frac{1}{2} + ik_\mathrm{B}Ts\right)\right\} \quad (3)$$

where ξ is the Riemann Zeta function and Γ is the gamma function.

Equation 3 is valid for different forms of the spectral density, but here, it is considered the Debye model of solids where the values of the parameters $p1$, $p2$, $p3$, and ω_C are $p1 = 1/2$, $p2 = 1/2$, $p3 = 2$, and $\omega_\mathrm{C} = \omega_\mathrm{D}$ (ω_D is the Debye frequency). Accounting for the Debye model in the eqs 2 and 2′ permits introduction of the frequency-dependent functions E_r and E_j

$$E_\mathrm{r} \equiv \frac{\hbar}{2}\sum_\mu \omega_\mu \Delta q^2(\omega_\mu) = 12{a_2}^2a_3\hbar{\omega_\mathrm{D}}^5 \qquad (4)$$

$$E_\mathrm{j} \equiv \frac{\hbar}{2}\sum_\mu \omega_\mu \frac{(J'_\mu)^2}{4} = 3{a_1}^2a_3\hbar{\omega_\mathrm{D}}^5 \qquad (4')$$

According to determination in ref 28, the value of E_r is the reorganization energy of the media. Using the formula

$$\xi(n,x) = \frac{(-1)^n}{(n-1)!}\Psi^{(n-1)}(x)$$

and eq 4, eq 4′ is possible to simplify the functions F_1, F_2, and F_3

$$F_1 = \frac{1}{12}\frac{E_j - E_r}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\Psi'''\left(\frac{k_BT}{\hbar\omega_D}\right) - \frac{1}{4}\frac{E_j - E_r}{\hbar\omega_D}$$

$$F_2(s) = \frac{1}{24}\frac{E_j + E_r}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\left[\Psi^{III}\left(\frac{1}{2} + \frac{k_BT}{\hbar\omega_D} - ik_BTs\right) + \Psi^{III}\left(\frac{1}{2} + \frac{k_BT}{\hbar\omega_D} + ik_BTs\right)\right] \quad (5)$$

$$F_3(s) = \frac{1}{12}\frac{\sqrt{E_jE_r}}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\left[\Psi^{III}\left(\frac{1}{2} + \frac{k_BT}{\hbar\omega_D} - ik_BTs\right) - \Psi^{III}\left(\frac{1}{2} + \frac{k_BT}{\hbar\omega_D} + ik_BTs\right)\right]$$

Here, $\Psi^{(n-1)}(x) - (n - 1)$ is the derivative of the digamma function $\Psi(x)$ ($n -$ whole number more than 1), where

$$\Psi(x) = \partial(\ln(\Gamma(x)))/\partial x$$

If one uses the expansions

$$\Psi^{III}\left(\frac{1}{2} + a + ix\right) \underset{x\to 0}{=} \Psi^{III}\left(\frac{1}{2} + a\right) + i\Psi^{IV}\left(\frac{1}{2} + a\right)x - \frac{1}{2}\Psi^{V}\left(\frac{1}{2} + a\right)x^2$$

$$x^4\Psi^{III}\left(\frac{1}{2} + x\right) \underset{x\to 0}{=} \pi^4x^4 - 744\xi(5)x^5 + 4\pi^6x^6$$

$$x^5\Psi^{IV}\left(\frac{1}{2} + x\right) \underset{x\to 0}{=} -744\xi(5)x^5 + 8\pi^6x^6$$

$$x^6\Psi^{V}\left(\frac{1}{2} + x\right) \underset{x\to 0}{=} 8\pi^6x^6$$

at low temperatures when $k_BT \ll \hbar\omega_D$, but at the same time, the inequality $3\Delta E(\hbar\omega_D/k_BT)^6/2\pi^6E_j \ll 1$ takes place, the expression for the tunneling rate constant can be found from eqs 3 and 5

$$k \sim \exp\left\{\frac{\Delta E}{2k_BT} + \frac{1}{4}\frac{(E_j - E_r)}{\hbar\omega_D} + \frac{\pi^4}{90}\frac{(8E_j + 7E_r)}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\right\} \quad (6)$$

If value of the reorganization energy is equal to zero ($E_r = 0$, $E_j \neq 0$), then

$$k \sim \exp\left\{\frac{\Delta E}{2k_BT} + \frac{1}{4}\frac{E_j}{\hbar\omega_D} + \frac{4\pi^4}{45}\frac{E_j}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\right\} \quad (6')$$

and at $E_j = 0$ ($E_r \neq 0$)

$$k \sim \exp\left\{\frac{\Delta E}{2k_BT} - \frac{1}{4}\frac{E_r}{\hbar\omega_D} + \frac{7\pi^4}{90}\frac{E_r}{\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)^4\right\} \quad (6'')$$

The power of the temperature in eqs 6′ and 6″ depends on the values of $p1$, $p2$, and $p3$ in eqs 2 and 2′. This power is equal to 4 only in the Debye approximation and may differ from 4 in the case of another dispersion low (cf. with ref 21). Equation 6″ corresponds to the rate constant of the electron tunneling in polar media and chemical conversions with a small influence of the intermolecular vibrations on the potential barrier of the reaction, for example, intramolecular transformations.

In the high-temperature range, $k_BT \gg \hbar\omega_D$, but as mentioned earlier, at $k_BT < \gamma_R/J''$, it is possible to find the rate constant from eqs 3 and 5 using the expansions

$$x^4\Psi^{III}(x) \underset{x\to\infty}{=} 2x + 3 + \frac{2}{x}$$

$$x^4\Psi^{III}\left(\frac{1}{2} + ia + x\right) \underset{x\to\infty}{=} 2x - 6ia - \frac{1}{x} - \frac{12a^2}{x}$$

The use of these expansions gives the expression for the rate constant of H-atom tunneling at high temperatures

$$k = \frac{1}{\hbar}|V(R_0)|^2\sqrt{\frac{\pi}{(E_j + E_r)k_BT}}\exp\left\{\frac{\Delta E\sqrt{E_jE_r}}{2(E_j + E_r)\hbar\omega_D}\right\} \times \exp\left\{\frac{6\Delta E(E_j + E_r) - 3E_r^{\ 3} - 2E_jE_r + E_j^{\ 2} - 3\Delta E^2}{12(E_j + E_r)k_BT}\right\} \times \exp\left\{\frac{4E_j^{\ 2} - E_jE_r}{12(E_j + E_r)\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)\right\}$$

This expression is complicated enough, but it can be essentially simplified in two cases. The first one is the possibility of neglect by the reorganization of the media and reagents

$$k = \frac{1}{\hbar}|V(R_0)|^2\sqrt{\frac{\pi}{E_jk_BT}}\exp\left\{\frac{6\Delta EE_j + E_j^{\ 2} - 3\Delta E^2}{12E_jk_BT}\right\} \times \exp\left\{\frac{E_j}{3\hbar\omega_D}\left(\frac{k_BT}{\hbar\omega_D}\right)\right\} \quad (7)$$

According to eq 7, the rate constant is mostly proportional to exp[α*T*]. This dependence is valid in a wide interval of temperatures[22,25] and, as shown in the refs 1, 4, and 25, transforms in the Arrhenius law at higher temperatures.

The second case is neglecting the parameter E_j (cf. with eq 6″)

$$k = \frac{1}{\hbar}|V(R_0)|^2\sqrt{\frac{\pi}{E_rk_BT}}\exp\left\{-\frac{(\Delta E - E_r)^2}{4E_rk_BT}\right\} \quad (8)$$

As mentioned earlier, this case is justified for electron transfer and intramolecular transformations. It is easy to see that eq 8 exponentially coincides with the well-known Marcus formula[30] for electron transfer but has never been deduced in the Debye approximation.

III. Comparison of Theoretical Results on the Temperature Dependence of the Rate Constant with Experimental Data

To the highest degree, the temperature and pressure dependence was studied for the intermolecular photosensitized tunneling of the H atom in the fluorene doped by acridine system.[9−15] This reaction was investigated in the very wide temperature (1.4−300 K) and pressure (0−35 kbar) intervals with great accuracy. The experimental conditions of this tunneling reaction are discussed next. In the first stage, the photoexcitation of the acridine molecule into a higher singlet state takes place. The second stage is the occupation of the lowest triplet state of this molecule as a result of intersystem crossing, and then, such an acridine state decays via two channels: the hydrogen atom transfers from the neighboring molecule of fluorene to the excited triplet state of acridine molecule, which results in a radical pair creation, and intramo-

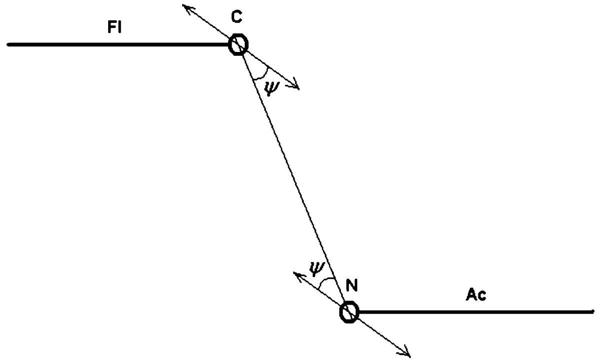

Figure 1. The scheme of the Fl−Ac reaction system. The ψ is the angle between two important directions; the first one is directed on the line connecting the C and N atoms in the fluorene and acridine molecules between which the H atom transfers, and the second one is the axis (↔) of the reagents' oscillations.

lecular radiative or radiationless transition to the ground electronic state. It is necessary to note that the fluorene and acridine molecules are practically equal in size and shape; therefore, this mutual crystal is an ideal crystal. This system was studied in a wide experimental pressure and temperature interval with great accuracy. The kinetics of this reaction is strictly exponential according to the first-order law. The important feature of the process is that there are four promotive modes affecting the rate constant of H-atom tunneling and its temperature and pressure dependence.

Recently, a comparison of the experimental data on the temperature dependence of the tunneling of the H atom in the fluorene−acridine system with the theoretical results was conducted.[26,27] The procedure of the comparison was described in details with use of the surface of the potential energy calculated by the PM3 (MOPAC)[31] and DFT-B3LYP/6-31G*[32] methods, taking into account four promotive modes, translational, librational, and two low-frequency intramolecular modes at 95 and 238 cm^{-1}, zero-point energy and tunneling parameters of the H atom.[26,27] The experimental and theoretical data were fitted in the whole investigated interval of temperatures and separately described at low (1.4−∼50 K) and high (∼50−300 K) temperature ranges. The results of calculations are coincided practically for the PM3 (MOPAC) and DFT-B3LYP/6-31G* surfaces of the potential energy. The single fitting parameter is the frequency of the translational mode; in the low-temperature range, the Debye frequency $\omega_D = 152 \div 155$ cm^{-1}, and in high-temperature range, the Einstein frequency $\Omega_T = 326 \div 350$ cm^{-1}. The experimental and theoretical results agree with good accuracy and c are lose to each other both for the low and high intervals of temperature. However, fitting frequencies are strongly differing for these two ranges. The reasonable explanations of this discrepancy proposed in the ref 27 are connected with anharmonicity, structural transitions, and interactions between promotive modes. As to the large value of the frequencies ω_D and Ω_T, it is necessary to take into account that the real positions of the reagents in the lattice are unknown.

Indeed, there are two important directions in the considered reaction system; one of them is directed on the line connecting the C and N atoms in the molecules fluorene and acridine, between which the H atom transfers, and the second one is the axis (↔) of the reagents' oscillations (Figure 1). The reaction center is the defect of the crystal lattice (despite the fact that the fluorene and acridine molecules are close in form and size). Therefore, it is impossible to recognize the real value of the angle ψ between these two directions from the crystal structure. Let us determine the angular dependence of the Debye fitting frequency ω_D. For that, the experimental temperature dependence $f_{exp}(T)$[9,10] of the tunneling rate constant in the range of 1.4−∼50 K compares with the theoretical exponent (eq 6′)

$$f_{exp}(T) = 4\pi^4 E_j \cos^2(\psi)(k_B T/\hbar\omega_D)^4/45\hbar\omega_D \tag{9}$$

Equation 9 determines the dependence of fitting frequency ω_D from the angle ψ. The results of fitting are presented in Figure 2a. It is easy to see that the frequency essentially decreases when the angle ψ increases. If a reasonable value of the Debye frequency is in the range of 50−60 cm^{-1}, the corresponding angle range is situated near $\psi = 75°$.

The analogous calculations at higher temperatures (∼50−300 K), with fitting formula

$$f_{exp}(T) = f_T(T) + f_{libr}(T) + f_{95}(T) + f_{238}(T) \tag{10}$$

where

$$f_{libr}(T) = \frac{1}{4}\frac{I\Omega_l^2 (J'_R)^2 \Delta_l^2}{I\Omega_l^2 + J'_R k_B T \partial^2 R/\partial\varphi_l^2} \coth\left(\frac{\hbar\Omega_l}{2k_B T}\right)$$

$$f_{T,95,238}(T) = \frac{(J'_R)^2}{4}\Delta^2_{T,95,238} \coth\left(\frac{\hbar\Omega_{T,95,238}}{2k_B T}\right)$$

$$\partial^2 R/\partial\varphi_l^2 = 0.51 \times 10^{-8}\text{cm} \qquad \Delta_T^2 = \frac{\hbar}{M\Omega_T}\cos^2(\psi)$$

$$\Delta_l^2 = 4.54 \times 10^{-2}\ \text{Å} \qquad \Delta_{95}^2 = 2.93 \times 10^{-2}\ \text{Å}$$

$$\Delta_{238}^2 = 3.86 \times 10^{-2}\ \text{Å} \qquad J'_R = 66.53\ 1/\text{Å}$$

give the range for Einstein translational mode $\Omega_T = 50-60$ cm^{-1} in the angle range close to $\psi = 85°$ (see Figure 2b). If

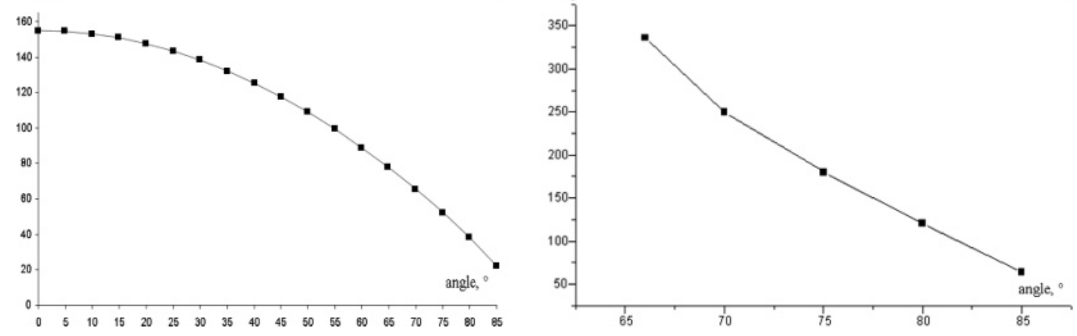

Figure 2. Dependence of fitting frequency from the angle between directions of the reagent oscillations and the line connecting the initial and final positions of the H atom; (a) low temperatures (1.4−∼50 K), and (b) high temperatures (∼50−300 K).

the values of fitting the intermolecular frequencies (ω_D, Ω_T) are greater, the corresponding angle ψ is less. It is not difficult to see that the determined values of the Debye and Einstein frequencies are reasonable and coincide with regular intermolecular frequencies for such kinds of crystals.

IV. Pressure Dependence of the Tunneling Parameters

The tunneling rate constant of the H atom is strongly dependent on the external hydrostatic pressure. As mentioned in section I, the volume and the linear sizes of a monocrystal elementary cell as well as the equilibrium distance between the reaction centers ($R_0(P)$) and the tunneling length decrease at the pressure action, and the tunneling rate constant sharply increases. Besides anharmonicity, the frequencies of the promotive modes $\Omega_l(P)$ also depend on pressure.

In the refs 11 and 13, the Murnaghan equation of state

$$P = a[(V_0/V)^b - 1] \qquad (11)$$

is used to estimate the pressure influence on the rate constant of tunneling. Parameters a and b equal to $a = 10.3$ kbar and $b = 7.3$[11] were obtained for the anthracene crystal.[33] The crystal lattice of anthracene has elastic and geometric characteristics similar to those of the fluorene one. For the simple cubic lattice, the volume which compresses uniformly on all directions under pressure action is given by the expression $R_0/R_{0P} \approx (V_0/V(P))^{1/3}$, where V(P) and V_0 are the monocrystal volumes at pressures P and the atmospheric pressure. As earlier,[27,34] the power 1/3 in this relationship is replaced by the factor η, which is considered as a fitting parameter. This approach allows one to take into account the fact that the volume occupied by a molecule compresses differently in comparison with the intermolecular volume. As a result, one can obtain the following relations for the equilibrium distance between the reagents

$$R_0(P) = R_0\rho^{-\eta}(P)$$
$$\rho(P) = V_0/V(P) = [(P/a) + 1]^{1/b} \qquad (12)$$

It is interesting to compare the above statement about different compressions of the molecule and the intermolecular volume with results of ref 11, where the rate constant of the fluorene−acridine reaction was measured at various temperatures and pressures. The absolute value of the rate constant increases as the pressure increases, but the change of this value differs for the low- and high-pressure ranges. It indicates that in these two pressure ranges, the tunneling length change occurs differentially. Indeed, in the low-pressure range, when only the intermolecular distance changes, the tunneling rate constant essentially grows with increasing pressure. At higher pressures, when the anharmonicity of the intermolecular interaction is considerable, a change of the intramolecular equilibrium coordinates plays an important role in reagent approachments, and the rate constant increase with pressure slows down. Of course, all of these peculiarities can taken into account by straight calculation of $R_0(P)$, but this is the very complicated way, and as earlier, the consideration will be restricted by the parameter η fitting.

Along with the different compression of the intra- and intermolecular space, there is one more complexity in the consideration of the pressure influence on the tunneling length in the fluorene−acridine system. The rigidity of the doped crystal along the longitudinal axis of the molecules is much smaller than that in the optimal direction for the reaction.[13] Therefore, the rigidity is different in different directions. In order not to complicate the fitting process, this additional effect of pressure is also included in the value η.

TABLE 1: Values of the Grueneisen Parameter for the Different Modes

mode	γ_l
translational vibration	0.200
librational vibration	2.038
intramolecular vibration (95 cm^{-1})	2.259
intramolecular vibration (238 cm^{-1})	0.400
Debye frequency (<150 cm^{-1})	1.274

The pressure dependencies of the frequencies of the promotive vibrations are expressed by the following empirical formula[13]

$$\Omega_l(P) = \Omega_l(V_0/V(P))^{\gamma_l} = \Omega_{l0}\rho^{\gamma_l}(P)$$
$$\gamma_l = -\partial \ln \Omega_l(P(V))/\partial \ln V \qquad (13)$$

Here, the value γ_l is the Grueneisen parameter for the mode l. According to ref 13, the values of the Grueneisen parameter for the considered system are in the Table 1. Taking into account that displacements of phonon coordinates are equal to $\delta_l^2 \sim 1/\Omega_l$, this is easy to find

$$\delta_l^{\,2}(P) = \delta_l^{\,2}\rho^{-\gamma_l} \qquad (14)$$

Another possibility of pressure action on the rate constant of atom tunneling can be due to the pressure dependence of the reorganization energy. It is clear, according to eq 4, that the reorganization energy depends on the Debye frequency and displacements of the phonon coordinates, which in one part depends on pressure eqs 12−14. Using these expressions, it is possible to obtain the pressure dependence of the reorganization energy; on the basis of eqs 4 and 2 and taking into account the proportionality

$$a_2^{\,2} \sim \Delta q_\mu^{\,2}(P) = \Delta q_\mu^{\,2}\rho^{-\eta_\mu}$$

the dependence of the reorganization energy on pressure may be found

$$E_{\boldsymbol{r}}(P) = E_r\rho^{5\gamma_D - 2\tilde{\eta}} \qquad E_r = E_r(P{=}0)$$

In this formula, the value $\tilde{\eta}$ is the effective parameter, which describes the resulting influence of pressure on displacements of the surrounding molecules and different atoms in the reagents (cf. with eq 12). The pressure dependence of the reorganization energy is presented in Figure 3. This dependence is strong

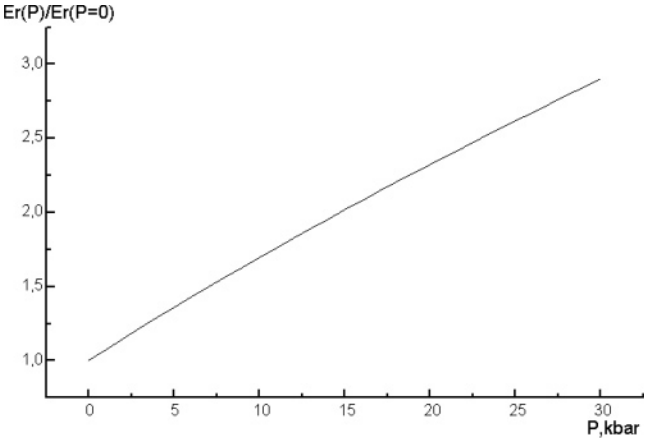

Figure 3. Pressure dependence of the reorganization energy.

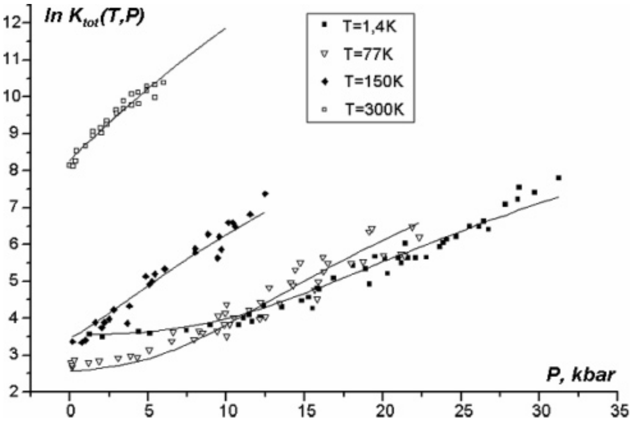

Figure 4. Pressure dependence of the summary rate constant of the triplet level decay. The experimental data[11−15] are represented by points (■ 1.4, ▽ 77, ◆ 150, and □ 300 K), and the curves are the theoretical results corresponding to eqs 15 and 16, with $K_{IC}(T) = 35$ s^{-1} at 1.4 K and $K_{IC}(T) = 13$ s^{-1} at other temperatures.

enough; the alteration of the external pressure up to 30 kbar leads to the 3× increase of the reorganization energy.

V. Comparison of the Theoretical Pressure Dependence of the Rate Constant with Experimental Data

The pressure dependence of the kinetics of fluorescence damping in the fluorene−acridine system was investigated experimentally[11−15] at the temperatures of 1.4, 77, 150, and 300 K (Figure 4). This kinetics corresponds to the two processes, pressure-dependent H-atom tunneling and practically independent pressure internal conversion

$$K_{tot}(T, P) = k(T, P) + K_{IC}(T)$$

Here, $k(T, P)$ and $K_{IC}(T)$ are the rate constants of tunneling and internal conversion. In our previous papers, the comparison of the experimental and theoretical data was conducted in two ways. The first one[34] is the summary rate constant $K_{tot}(T, P)$, that is, the direct results of the experiments[9−15] were compared with the theory. In the second case,[26,27] the contribution of the tunneling rate constant $k(T, P)$ into the experimentally measured summary rate constant $K_{tot}(T, P)$ was determined using the isotope effect[35] and then compared with the theory. It was found that the second way is more productive for description of the temperature dependence of the rate constant than the first one because, in this case, all peculiarities of the theoretical and experimental curves have the corresponding physical sense. This procedure was described in details in a recent paper.[27] As for the pressure dependence of $K_{tot}(T, P)$, the value of $K_{IC}(T)$ does not depend on the pressure. For this reason, the summary rate constant $K_{tot}(T, P)$ is used for the comparison of the experimental and theoretical data.

Using the pressure dependencies of the parameters in eqs 12−14, eq 6″, and the results of the ref 27, it is possible to find the expression for the tunneling rate constant as a function of temperature and pressure. At low temperatures ($T < 50$ K), in the Debye approximation

$$k(T,P) = \check{K}_0 \exp\{J_R{}^{I}\cdot R_0(1 - \rho^{-\eta})\} \exp\left\{\frac{\alpha T^4}{\rho^{5\gamma_D}}\right\} \tag{15}$$

Here, γ_D is the Grueneisen parameter for the Debye frequency ($\gamma_D = 1.274$)[13] (see also Table 1), and $\check{K}_0 = k(T{=}0, P{=}0) = 0.3$ s^{-1}.

At higher temperatures ($T > 50$ K)

$$\begin{aligned} k(T,P) = {} & K_0 \exp\{-J(R_0(P))\} \times \\ & \exp\left\{\frac{1}{4}(J'_R)^2 \sum_l \delta_l{}^2(P)\left(\frac{\partial R}{\partial \varphi_l}\right)^2 \coth\left(\frac{\hbar\Omega_l(P)}{2k_BT}\right)\right\} \\ = {} & \tilde{K}_0 \exp\{J_R{}^{I}\cdot R_0(1 - \rho^{-\eta})\} \times \\ & \exp\left\{\frac{1}{4}(J'_R)^2 \sum_l \rho^{-\gamma_l}\delta_l{}^2\left(\frac{\partial R}{\partial \varphi_l}\right)^2 \coth\left(\rho^{\gamma_l}\frac{\hbar\Omega_l}{2k_BT}\right)\right\} \end{aligned} \tag{16}$$

The preexponential factor is

$$\tilde{K}_0 = k_0 \times \frac{0.3c^{-1}}{\exp\left\{\frac{1}{4}(J')^2 \sum_l \delta_l{}^2\left(\frac{\partial R}{\partial \varphi_l}\right)^2\right\}}$$

Equations 15 and 16 depend on parameters of the reaction system; some of them were known earlier and used for considering the temperature dependence of the rate constant. The translational frequency has been found in ref 27 (see also section III). There are two new fitting parameters k_0 and η for the description of the pressure effect on the tunneling rate constant. These parameters were selected (see Table 2) according the fitting procedure to minimize the sum of the squares of the deviations between the experimental and theoretical points. In Figure 4, theoretical dependences (eqs 15 and 16) on the parameters given in Tables 1 and 2 are represented by continuous curves. The results of the fitting demonstrate the good description of the experimental data. Notice that at $T = 300$ K, H-atom transfer occurs most likely not only by the tunneling.

The detailed explanations of the peculiarities of the reaction in the fluorene−acridine system at $T = 300$ K were presented in ref 27. The first feature consists of the possibility of phase transitions in the fluorene matrix at room temperature under pressure action, and another one is the contribution of the classical overbarrier H-atom transfer. In the case of the classical mechanism of the reaction, the equality $J'' = 0$ does not fulfill, and the temperature dependence of the rate constant is much more complicated than eq 1.[1,25] The value of the parameter η at $T = 300$ K also indicates the contribution of classical transfer. Indeed, at $T = 1.4$, 77, and 150 K, the parameter η is less than 1/3, as it must be if only part of the reaction volume diminishes. Quite the contrary, at $T = 300$ K, the parameter $\eta > 1/3$. It means that tunneling eq 16 is not true for the real mechanism of atom transition.

TABLE 2: Fitting Values of Parameters η and k_0 in the Dependence of Temperature

η ($T = 1.4$ K)	η ($T = 77$ K)	k_0 ($T = 77$ K)	η ($T = 150$ K)	k_0 ($T = 150$ K)	η ($T = 300$ K)	k_0 ($T = 300$ K)
0.197	0.253	0.40	0.253	1.05	0.36	0.22

Besides, the preexponential factor k_0 has a weak temperature dependence, with the maximum near $T = 150$ K. It may be caused by the reorganization of media induced by the reaction. Since the reorganization energy in this reaction system is small, the influence of the media reorganization on the rate constant is manifested in a slight dependence of k_0 on T. Besides, as mentioned earlier, the essential role may be in phase transitions, which can give the maximum in the temperature dependence of the preexponential factor k_0 near $T = 150$ K.

VI. Conclusions

The analytical expression of a rate constant of a chemical reaction with an atom tunneling transfer is found for a continuous spectrum of the phonon subsystem in the frame of the modified theory of radiationless transitions. Two mechanisms of temperature dependence of a rate constant, (a) the oscillations of the potential barrier of the reaction at the intermolecular vibrations and (b) media reorganization, are taken into account. The simple expressions for temperature dependencies of a rate constant are obtained for the special case of lattice motion—the Debye model. At low temperatures, the logarithm of a rate constant is mainly proportional to T^4 for both mechanisms. At high temperatures, the logarithm k is proportional to T in the case of classical intermolecular vibrations for the (a) mechanism of temperature dependence. Another mechanism (b) gives the well-known Marcus expression for the rate constant of an electron transfer. The standard procedure of this formula is based either on the Einstein or the classical model of media. The expression of the Marcus formula for the continuous phonon spectrum is deduced first.

The pressure dependence of the rate constant of atom tunneling is considered. First, the pressure dependencies of the tunneling distance and promotive frequencies are found in the case when the Grueneisen parameters are different for different frequencies and the analytical expression of the energy reorganization as a function of external pressure is given. The comparison of the theoretical results with the literature experimental data[9−15] on H-atom tunneling in the fluorene−acridine crystal is fulfilled. Here, four promotive modes (translational, librational, and two low-frequency intramolecular modes at 95 and 238 cm^{-1}) and the frequency dependence of the Grueneisen parameter are taken into account. The system parameters, which are used for the fitting procedure, were obtained from the semiempirical PM3 and density functional B3LYP potential energy surfaces calculated earlier.[26,27] As a result, good agreement of the theory and experiments is observed.

Note that although this paper deals with chemical reactions in the solid phase, such mathematical techniques, especially in the Einstein approximation, as mentioned in the refs 36 and 37, are applicable to the description of the processes of atom and charge transfer in liquids.

Acknowledgment. The authors are grateful to Professors Sheng H. Lin and Aleksandr M. Mebel for constructive discussion of this material. In part, this work is supported by the Contract 02.513.11.3177 of the Federal Agency for Science and Innovations.

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